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Pressure Induced Bonding Changes in Carbon Dioxide: Six Fold Coordinated CO₂

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FY07 LDRD Final Report
**Pressure Induced Bonding Changes in Carbon Dioxide:
Six Fold Coordinated CO₂**

LDRD 07-LW-049

Valentin Iota, Principal Investigator

Abstract

In this LDRD, we examined in detail the pressure-induced bonding and local coordination changes leading to the *molecular* → *associated* → *extended-solid* transitions in carbon dioxide (CO₂). We studied the progressive delocalization of electrons from the C=O molecular double bond at high pressures and temperatures, and determined the phase stability and physical properties of a new extended-solid CO₂ phase (VI). We find that the new CO₂ phase VI is based on a network of six-fold coordinated (octahedral) CO₆ structures (similar to the ultra-hard SiO₂ phase *stishovite*).

Introduction/Background

At pressures below 10GPa, CO₂ is a prototypical simple molecular solid, stabilized by strong π bonding within the linear-symmetric molecules, and relatively weak quadrupolar intermolecular interactions. At high pressures and temperatures, however, CO₂ transforms to a series of solid polymorphs with differing intermolecular interactions, chemical bonding and crystal structure. Important here is the extended covalent solid (polymeric) CO₂-V, formed above 35 GPa and 1800 K. Its structure is based on corner sharing CO₄ tetrahedra, similar to that of SiO₂ tridymite.

One of the important questions we explored in this study was the existence of additional CO₂ extended-solid polymorphs, in particular, the stability of a 6-fold coordinated solid – equivalent to SiO₂ stishovite.

Research Activities

We explored the phase diagram of CO₂ at pressures up to 100GPa and temperatures up to 3000K by using heated diamond anvil cells (DAC). Experiments up to 1000K used external (resistive) heating coils wrapped around the DAC, whereas laser heating techniques were used above 1000K.

The phase stability and physical properties of CO₂ samples were determined *in situ* by a combination of RAMAN spectroscopy and X-ray diffraction measurements. In addition, we used X-ray Raman Spectroscopy measurements on quenched samples to determine the bonding characteristics of the resulting CO₂ phases.

Results/Technical Outcome

Our study established the stability and physical properties of a new covalent CO₂ phase formed by compressing the intermediate phase II at pressures above 50GPa and temperatures above 550K. Raman and XRD measurements show that the structure of CO₂-VI is based on six-fold coordinated C (octahedral C-O units) similar to the Si-O arrangement in stishovite. In addition, we derived a new phase diagram for carbon dioxide, based on the bonding changes in CO₂ from molecular to intermediate phases and finally to fully covalent phases at higher pressures.

Summary

This LDRD studied in details the phase/structural/bonding phase diagram of CO₂ - a prototypical molecular crystal – at high pressure and temperature. Our results are important beyond CO₂ – improving our understanding of pressure-induced bonding changes in molecular solids.

Publications:

1) Six-fold coordinated carbon dioxide VI, V. Iota, CS. Yoo, JH. Klepeis, Z. Jenei, W. Evans and H. Cynn, *Nature Materials* **6**, 34 (2007)

Invited Presentations:

1) *Bonding Changes in Compressed Carbon Dioxide: A New Stishovite-like Phase of CO₂*
APS March Meeting, March 2007, Denver, Colorado

2) *Bonding Changes in Compressed Carbon Dioxide*, SMEC conference, Miami Beach, April 2007

3) *Bonding and coordination changes in compressed carbon dioxide*, Joint 21st AIRAPT and 45th EHPRG International Conference on *High Pressure Science and Technology*, Catania, Italy, September 2007

4) *A New Six-fold Coordinated Covalent Phase of CO₂*, APS DOE Technical Review, Argonne National Laboratory, 2008